

Future Materials Issues for Synchrotron Science

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*A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago*



Goals

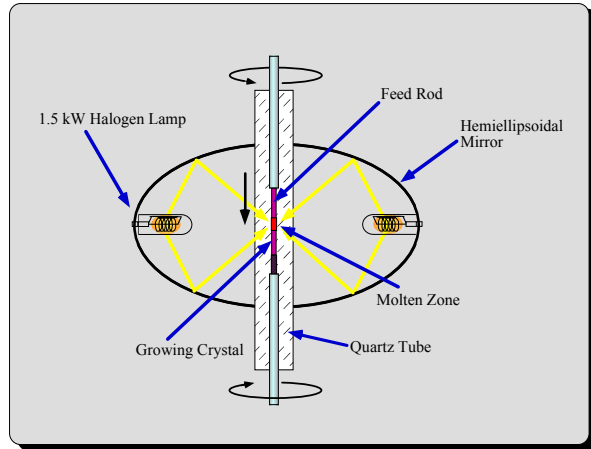
Highlight some ways that synchrotron x-rays might help the materials grower

Suggest some possible materials directions that will impact correlated electron studies

Floating-Zone Crystal Growth

Advantages

- Containerless growth = reduced contamination
- Large (cm^3) crystals can be obtained
- Excellent for high melting point materials (e.g., oxides)
- Huge success list: cuprates, manganites, titanates, vanadates, cobaltites, ruthenates, etc.

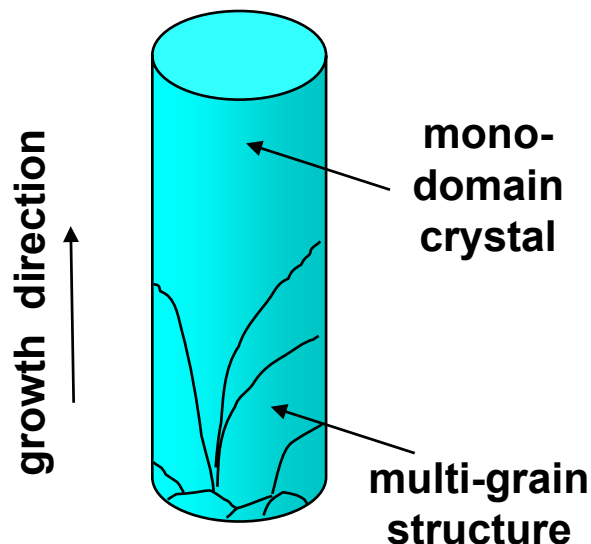


QuickTime™ and a YUV420 codec decompressor a

How SXR Might Help

- Real time monitoring of crystal growth
- “Phase spread” analysis
- Analysis of small crystallites

Real Time Monitoring of Crystal Growth

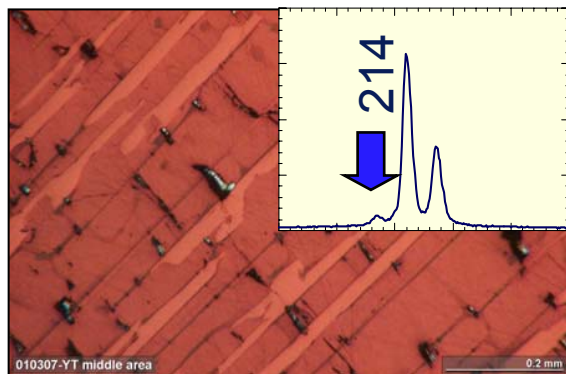


Can a FZ furnace be put on a beamline? If so, should it be?

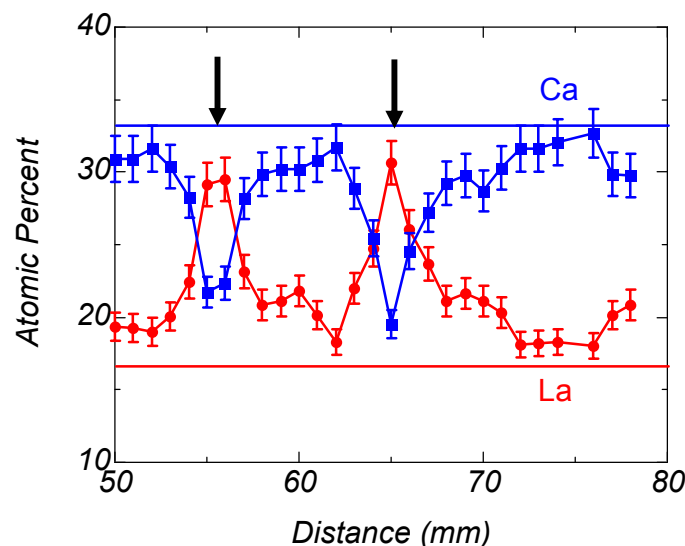
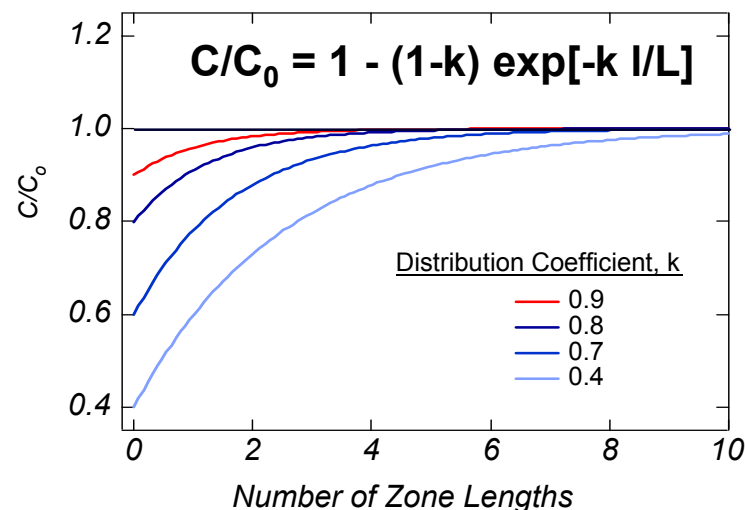
- Image or monitor grain development and growth
- Know immediately if second phases are precipitating
- Real time composition analysis with high spatial resolution

Examples:

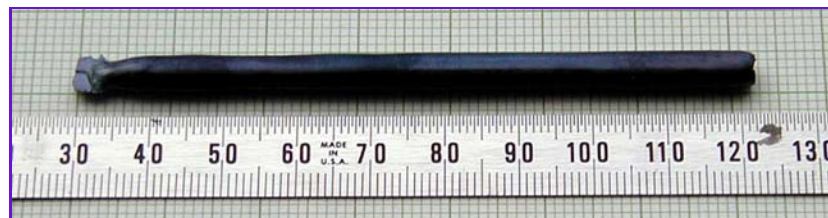
- ESRF ID-19 $\text{KAl}(\text{SO}_4)_2$ xtal topographic monitoring
- Lysozyme growth [Acta Cryst. 95, 650 (1999)]
- APS MOCVD ferroelectric films



Exploiting the Zone Distribution



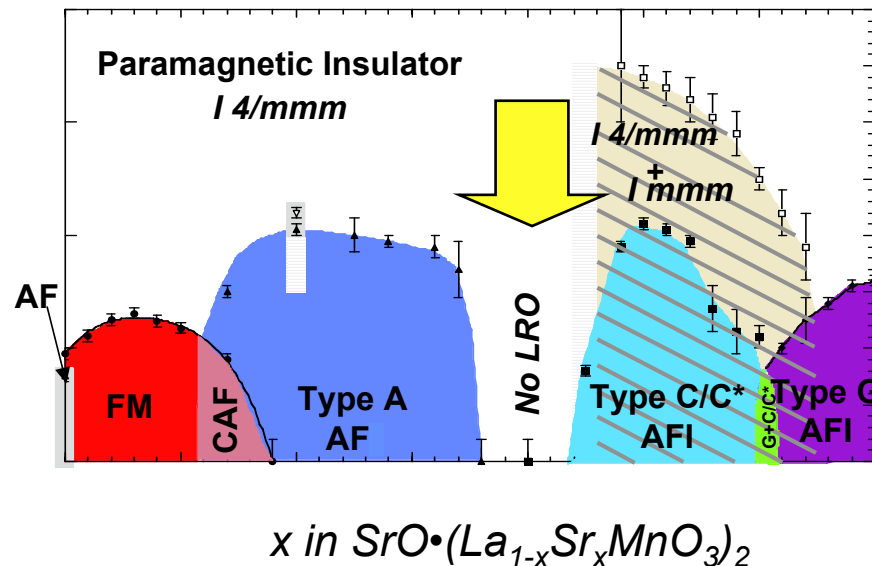
We like to study doped crystals



- For homogeneous crystals, we want to $C/C_0 \sim 1$
- Opportunity to study “phase spread” in a single growth
- Need high spatial resolution, means to validate chemistry

Why?

Phase diagram of bilayer manganites, $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$

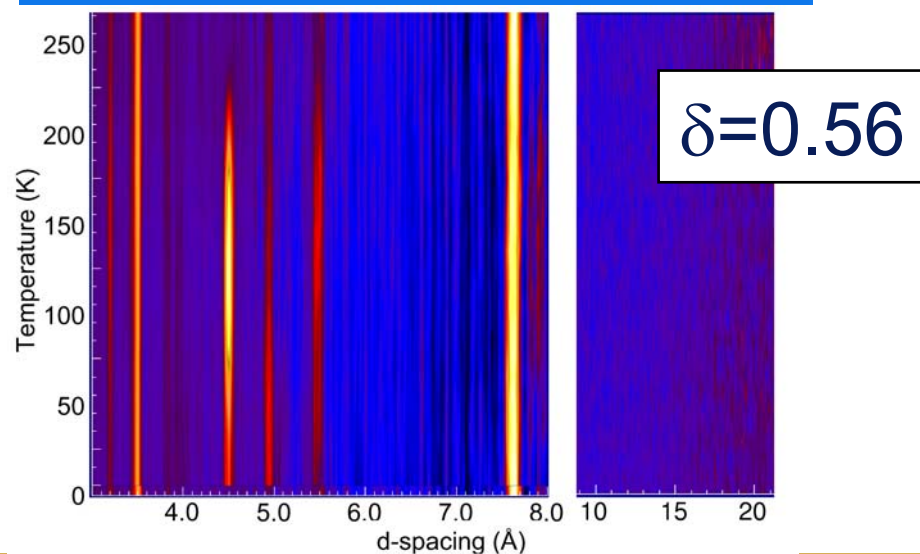
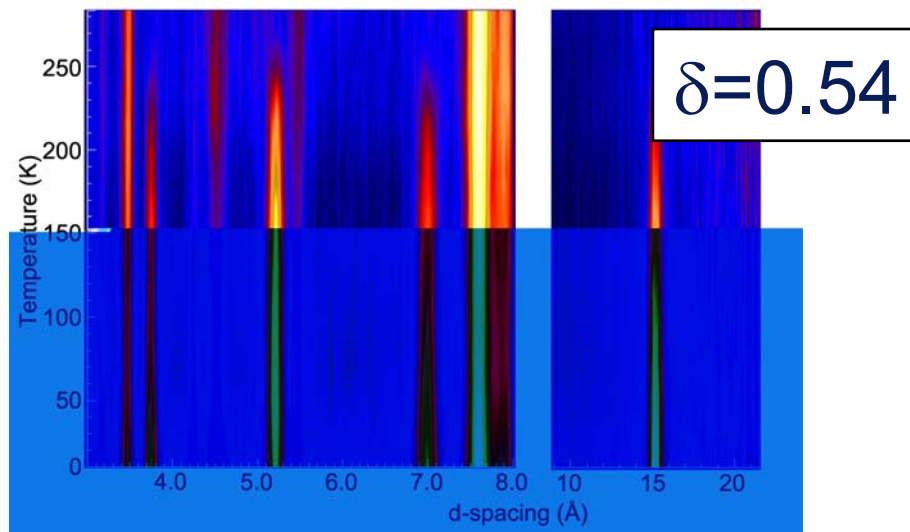
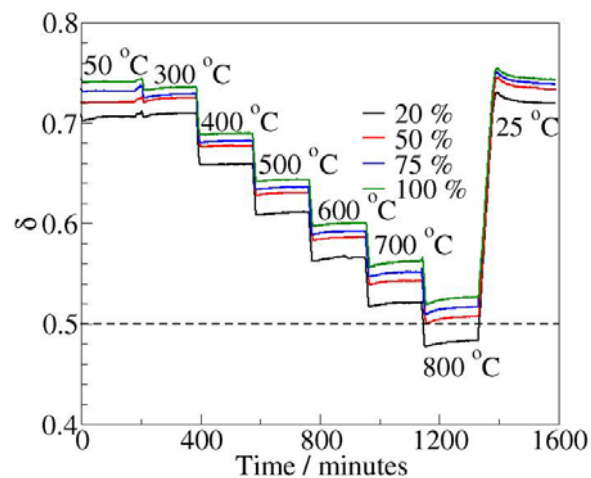
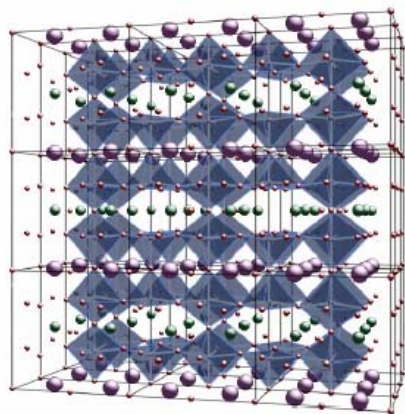


- Large crystals for $x < 0.6$
- “junky” crystals for $x > 0.6$
- But this is a really interesting area!

- Magnetic structures
- Diffuse magnetic scattering (element specific)
- Competition with SNS?

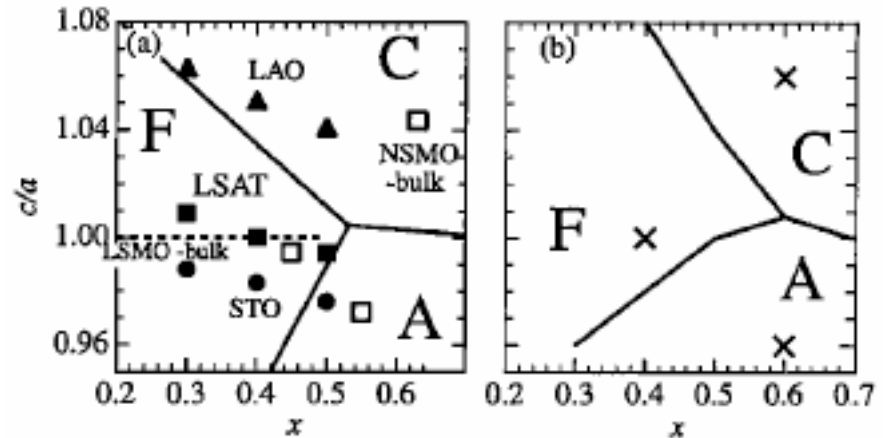
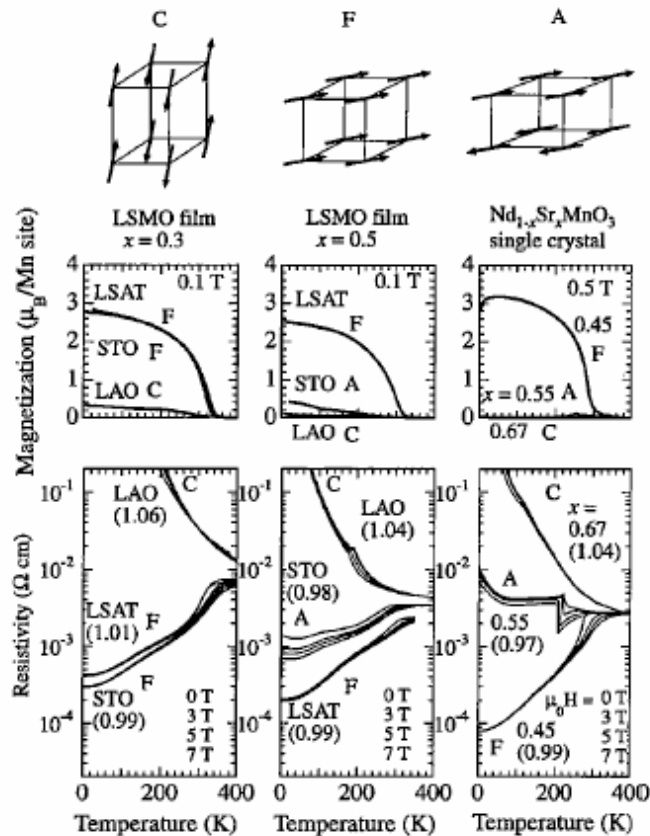
Extreme Sensitivity to Oxygen Content, Order

Spin states in Co^{3+} compounds



Hybrid Materials: Control of Interface Orbital Polarization

Y. Konishi et al. JPSJ 68, 3790 (1999)

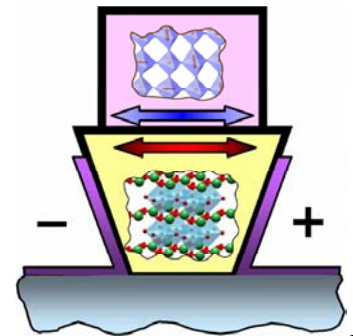


SXR Opportunities:

- Interface magnetism
- Resonant scattering - OO at interfaces?

Put complex materials on same footing as metallic multilayers

Active Control:



Prototype CMR-Piezoelectric Hybrid

D. Dale et al. APL 82, 3725 (2003)

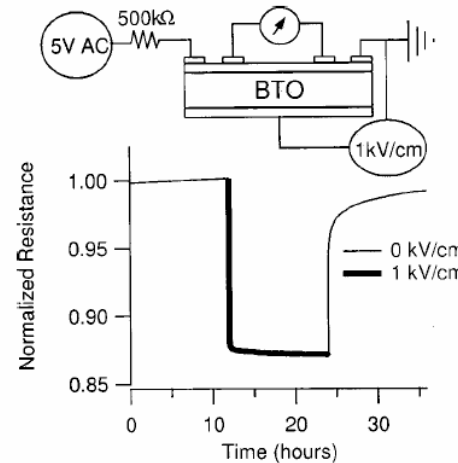
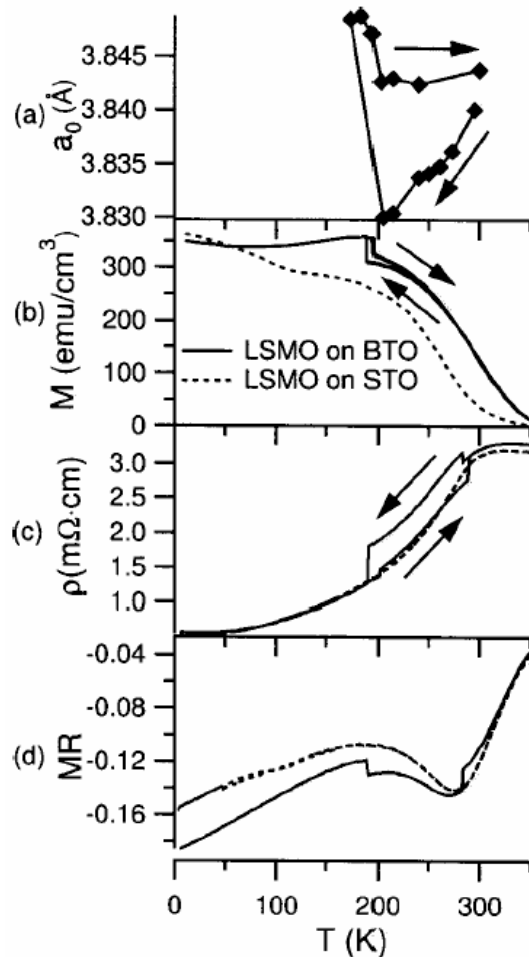


FIG. 2. R vs time, measured along the in-plane $\langle 100 \rangle$ of LSMO on BTO. The 1 kV/cm poling field was turned on and off at 12 and 24 h, respectively.

Poling of BaTiO₃ (BTO) piezoelectric results in decreased resistivity.
SXR Opportunity: Need to better understand complexity of the interface, since BTO twinned.

Field-Effect Doping: C.Ahn et al. *Nature* Aug 28, 2003

Alternative Materials Opportunities

Metal-Insulator Transition

Charge Order

Magnetism

Spin-Peierls Transition

Ferroelectricity

Superconductivity

Magnetoresistance

Doping

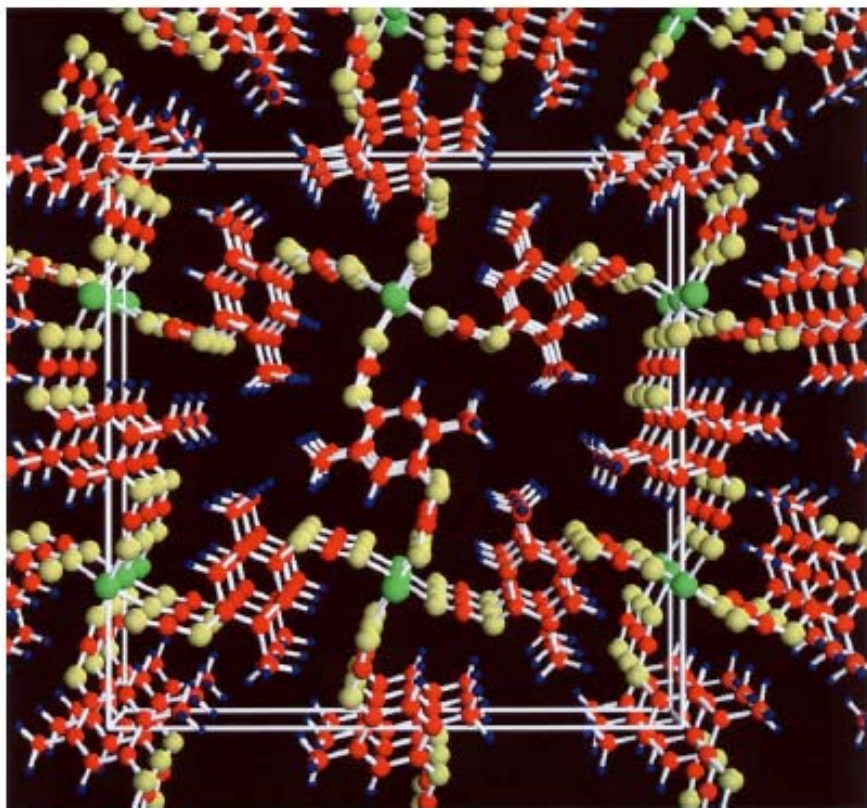
Structural modifications

Response to fields

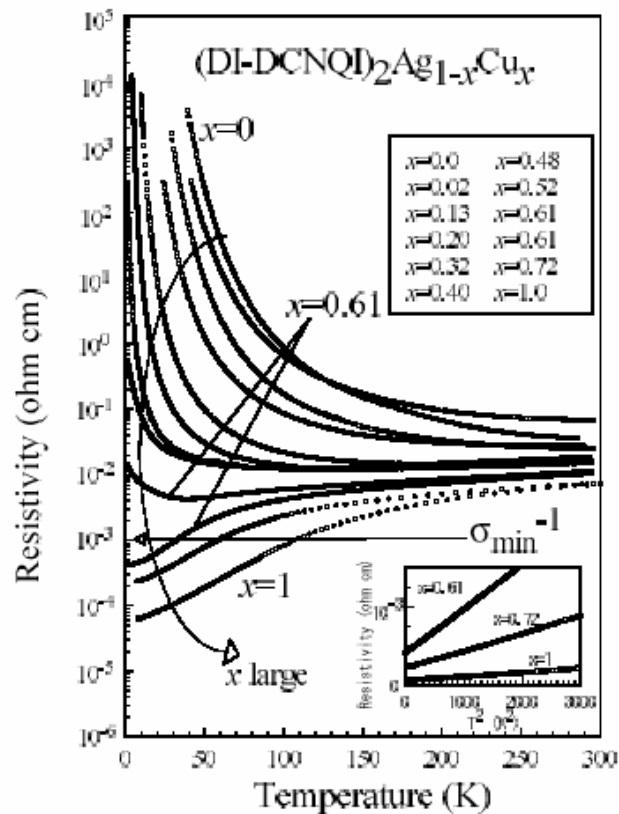
~~Transition Metal
Oxides~~

Organics!

d-Orbital “doping” in 1-D $(DI-DCNQI)_2Ag_{1-x}Cu_x$

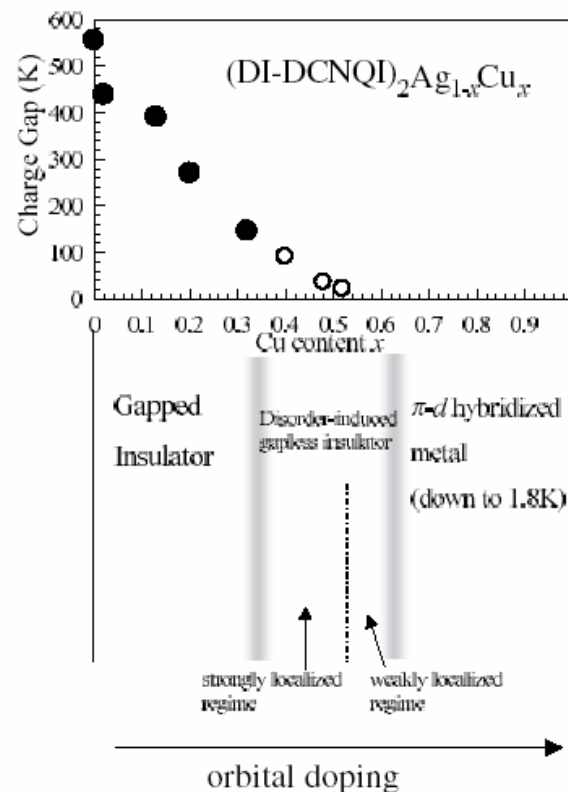
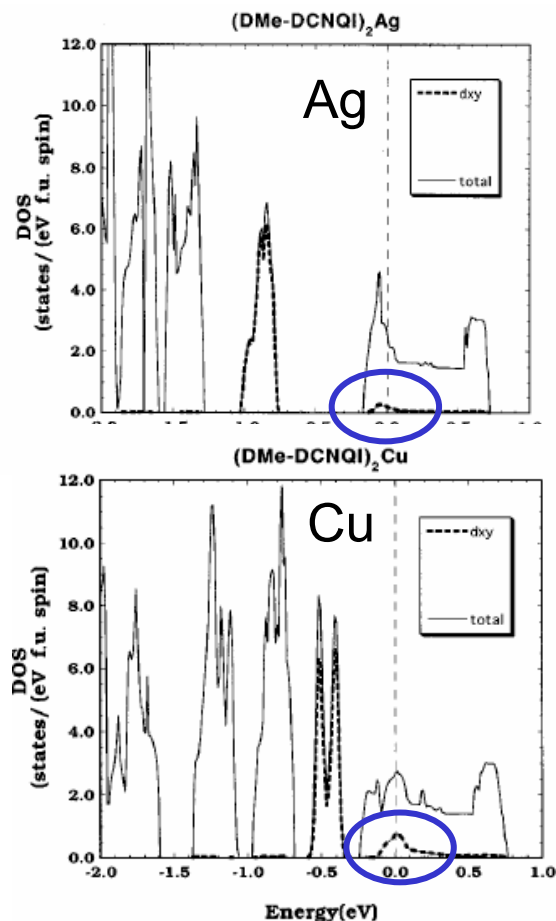


- Molecules stack parallel to c
- Metal links chains in 3-D
- MIT as function of Ag/Cu



d-Orbital “doping” in 1-D $(DI-DCNQI)_2Ag_{1-x}Cu_x$

T. Itou et al. PRL 889, 246402 (2002)



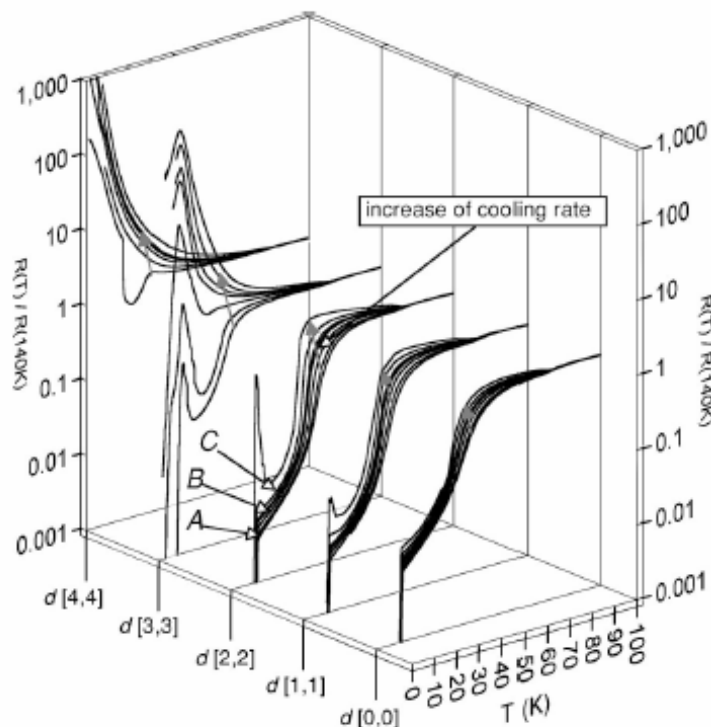
Cu^+ d to organic π manifold
better overlap than Ag^+ =
more three-dimensional

π - d states in Coulomb-gapped insulator

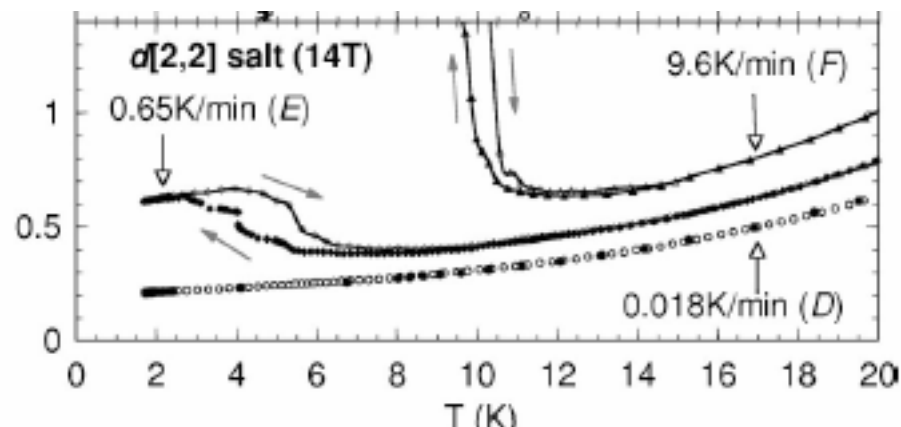


Phase Control by Chemical Modification

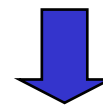
Modifying deuterium content in κ -(BEDT-TTF)₂[N(CN)₂]Br drastically impacts electronic states



H. Tanaguchi et al. PRB 67, 014510 (2003)



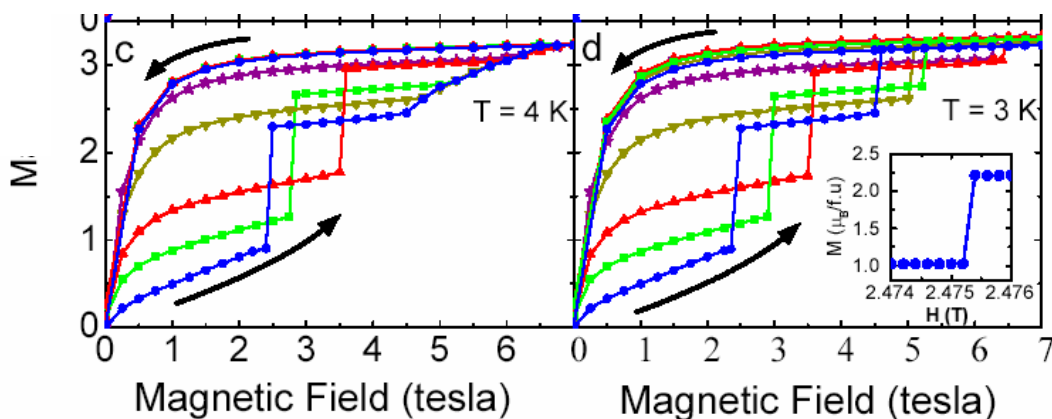
Cooling Rate Dependence in High Field
Slow: Superconductor - Metal
Fast: Superconductor - Insulator



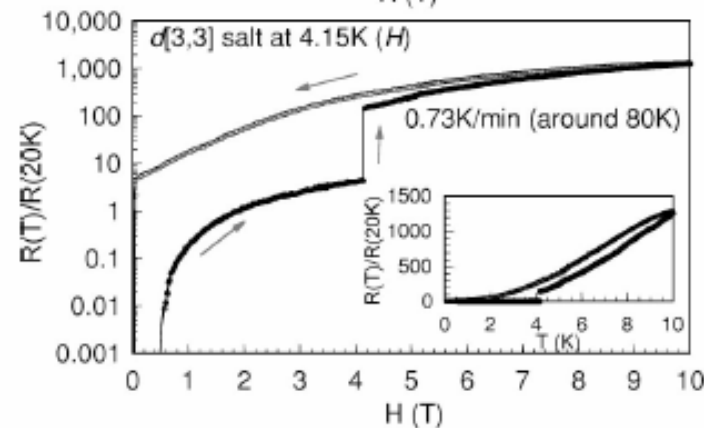
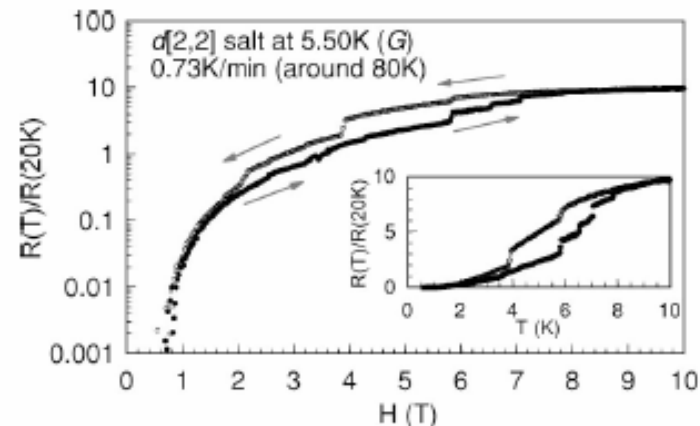
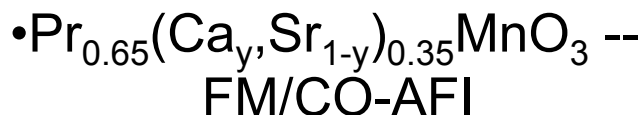
Subtle rearrangement of
BEDT-TTF impacts U/W near
first order SC-AFI boundary

Organics and Manganites: A Parallel?

Mahendiran et al. PRL 89, 286602 (2002)



Ultra-sharp magnetization steps
reflect phase segregation



Organic salt --
AFI/PM (?)

An Opportunity for Synchrotron Science

Experiments Related to Organics/Correlated Electrons
(includes fullerenes)

	1999	2000	2001
ALS	1	1	6
APS	0	3	2
NSLS	?	4	?
SSRL	?	4	2
Synth. Met. (ISI count)	1466	445	1348

Source: Data available at facility websites (Activity Reports, Publication Lists)

Summary

Symbiosis between materials growth and scattering science

- Push envelope in in-situ studies of xtal growth
- Don't rely on cm^3 crystals
- Bring bulk science to interfaces
- Look beyond traditional “hard” materials --
Organic chemistry is extremely rich, high level of stoichiometry, structure control